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(54) Process for the production of filter elements based on polysulphone

(57) In the production of polysulphone-based filter elements cell structure reproducibility is improved by carrying out coagulation and stabilization of the polysulphonate solution in a liquid bath over a period of about 30 seconds to 240 seconds,

a) at temperatures from below 0°C to about 15°C for producing filter elements of pore size 0.1 nm to 1 nm suitable for the separation of macromolecules (ultrafiltration), or

b) at temperatures from about 15°C to about 45°C for producing filter elements of asymmetric cell structure and pore size 0.05 μm to 10 μm suitable for the separation of particles (microfiltration) or

c) at temperatures from about 45°C to 80°C for the production of filter elements of a symmetric cell structure and a pore size 0.05 μm to 10 μm for the separation of particles (microfiltration),

the filter element being subsequently washed in a liquid bath.

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Fig.1

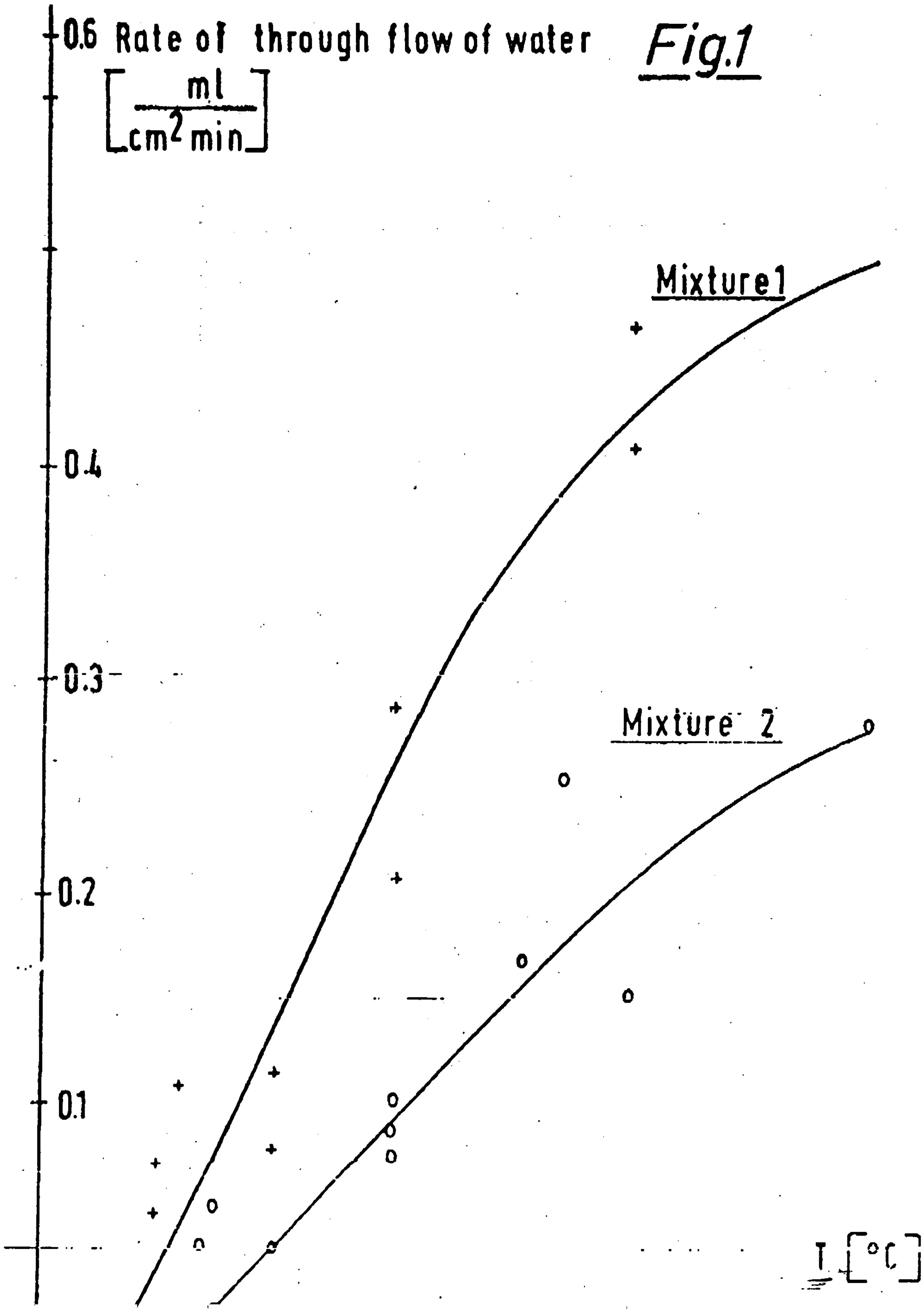
0.6 Rate of through flow of water
[ml/cm2 min]
Mixture 1
Mixture 2
0.4
0.3
0.2
0.1
T [°C]

Fig.2

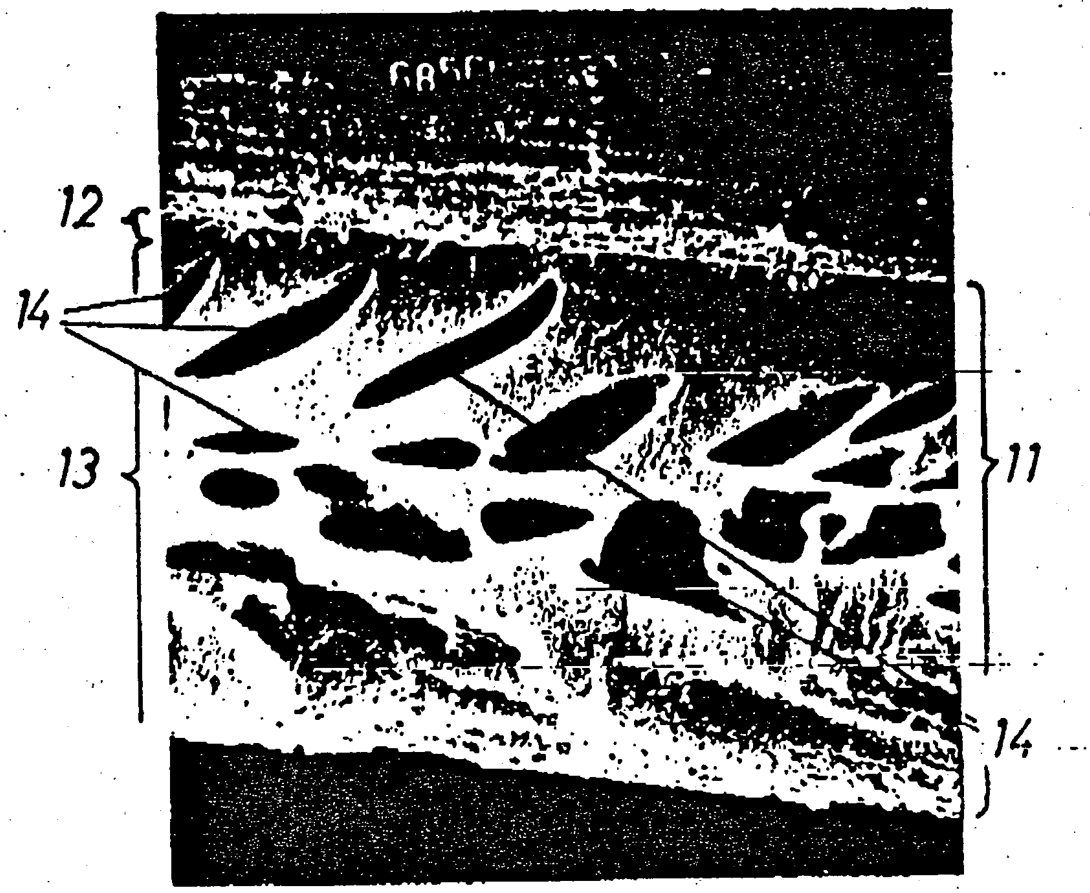

Fig.3

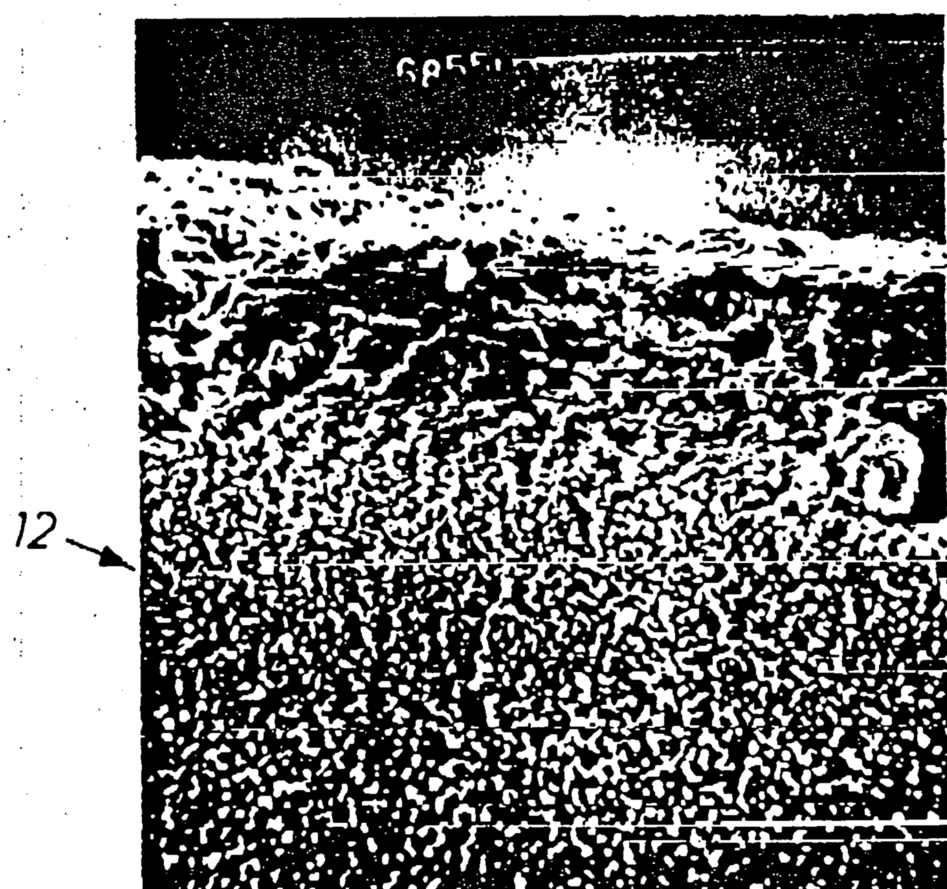

Fig.4

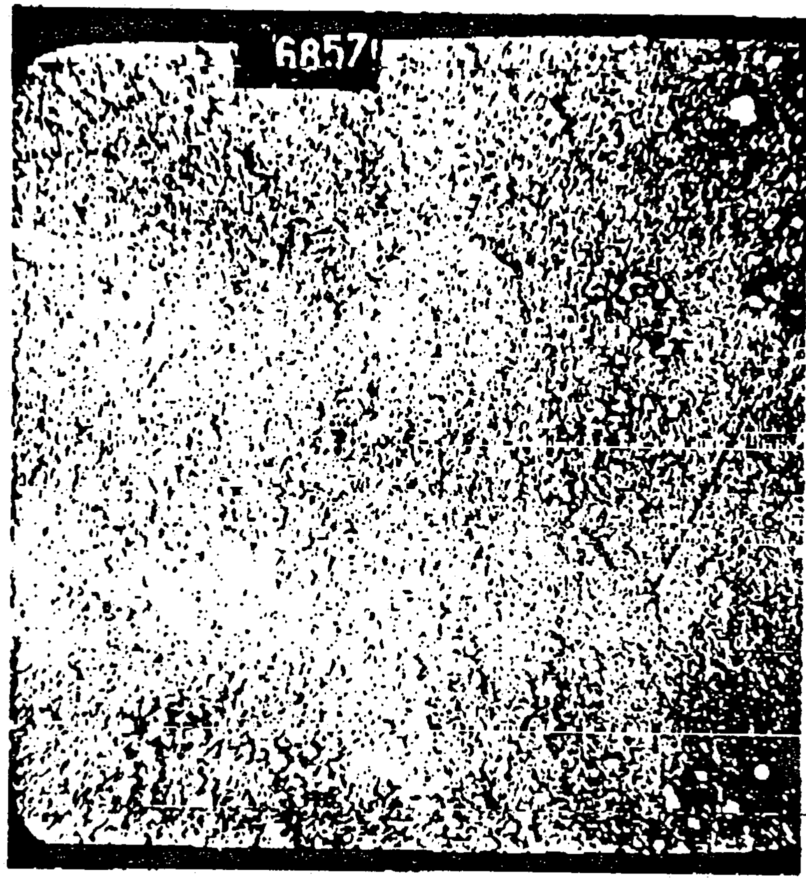

Fig.5

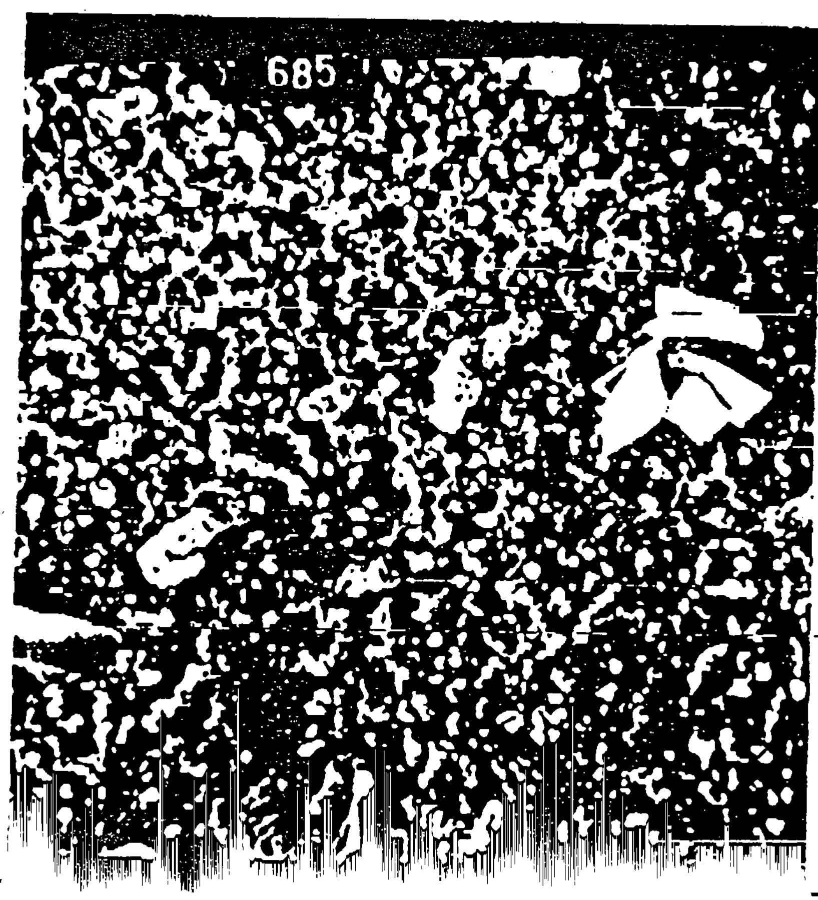

Fig.6

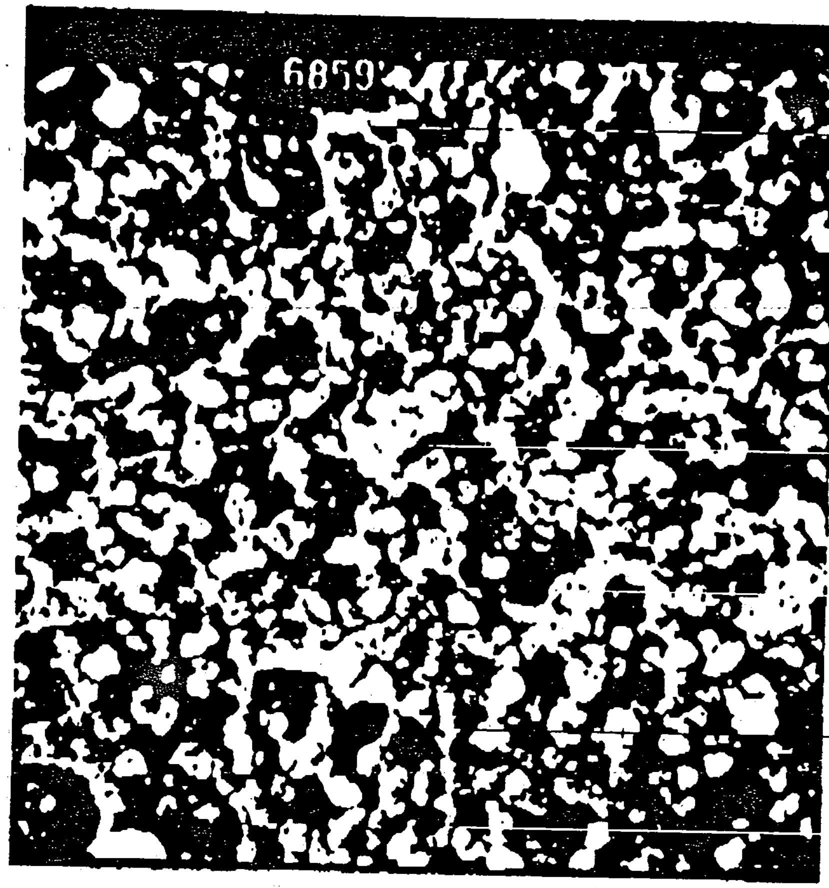

Fig. 7

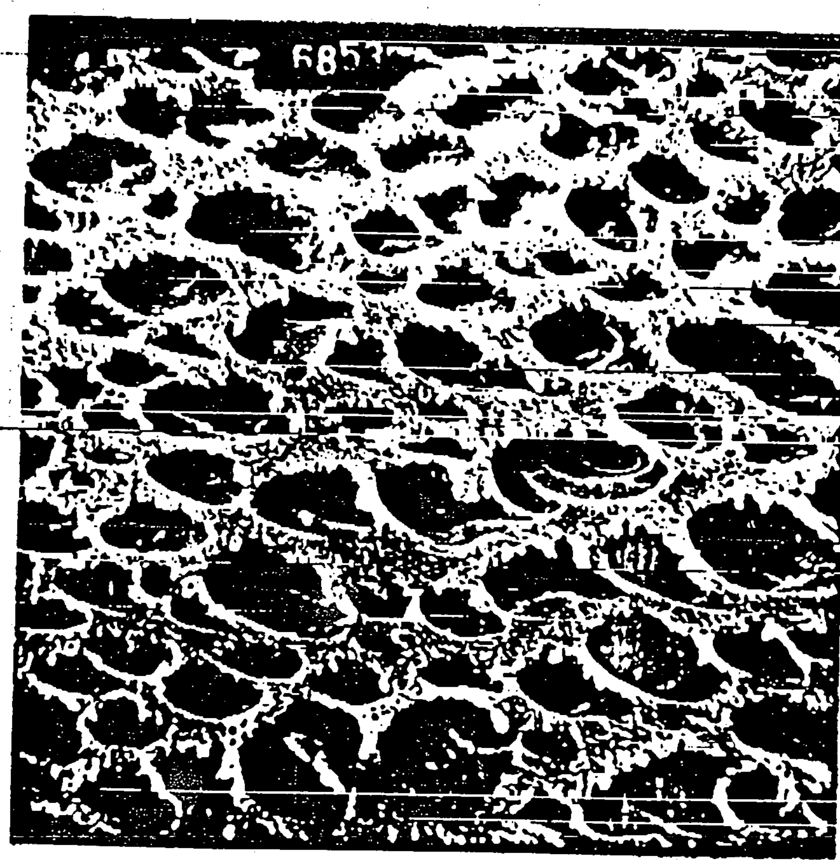

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Fig.8

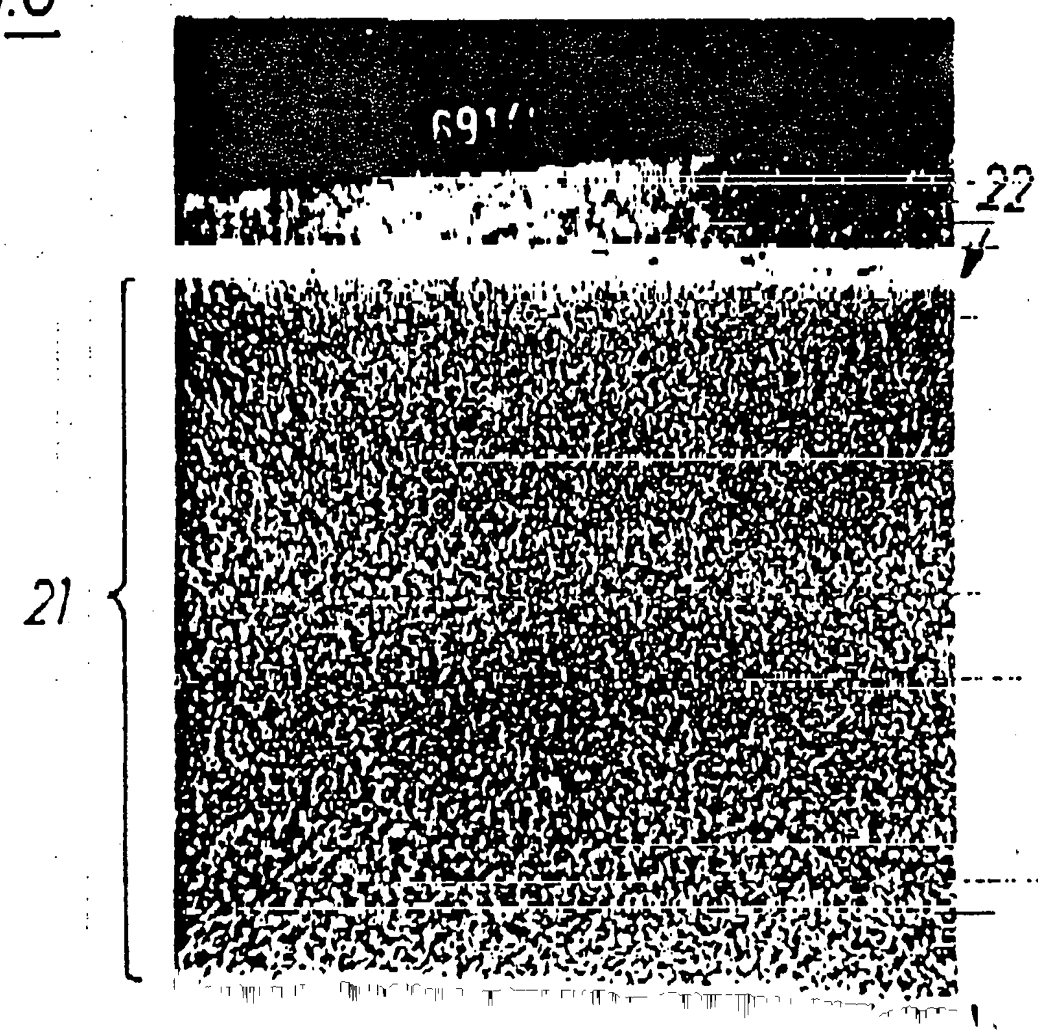

Fig.9

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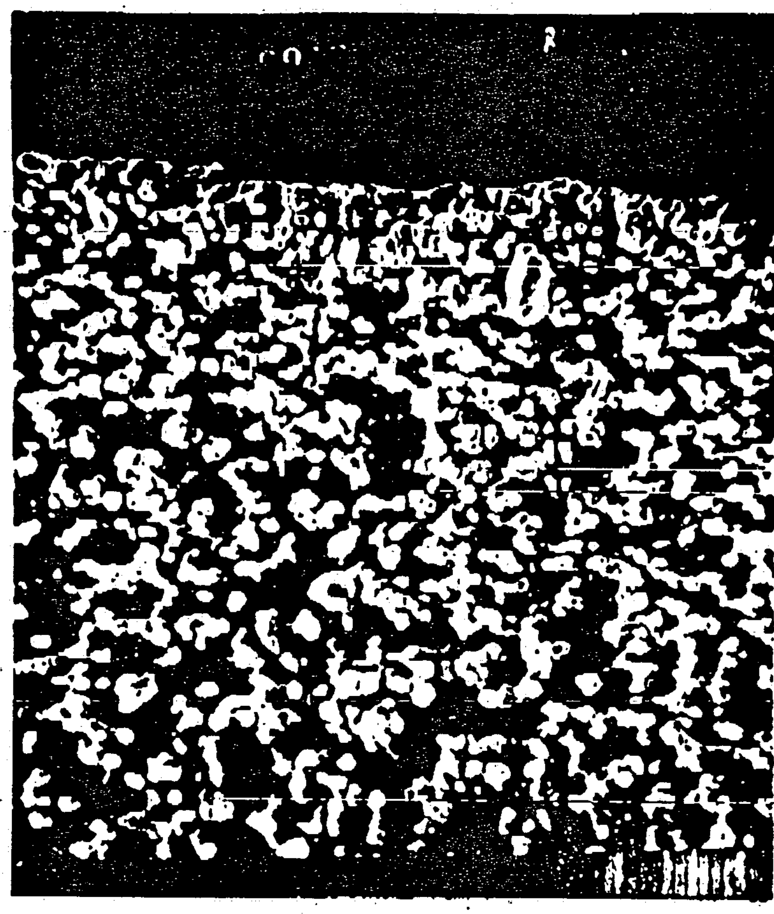


Fig.10

23

Fig.11

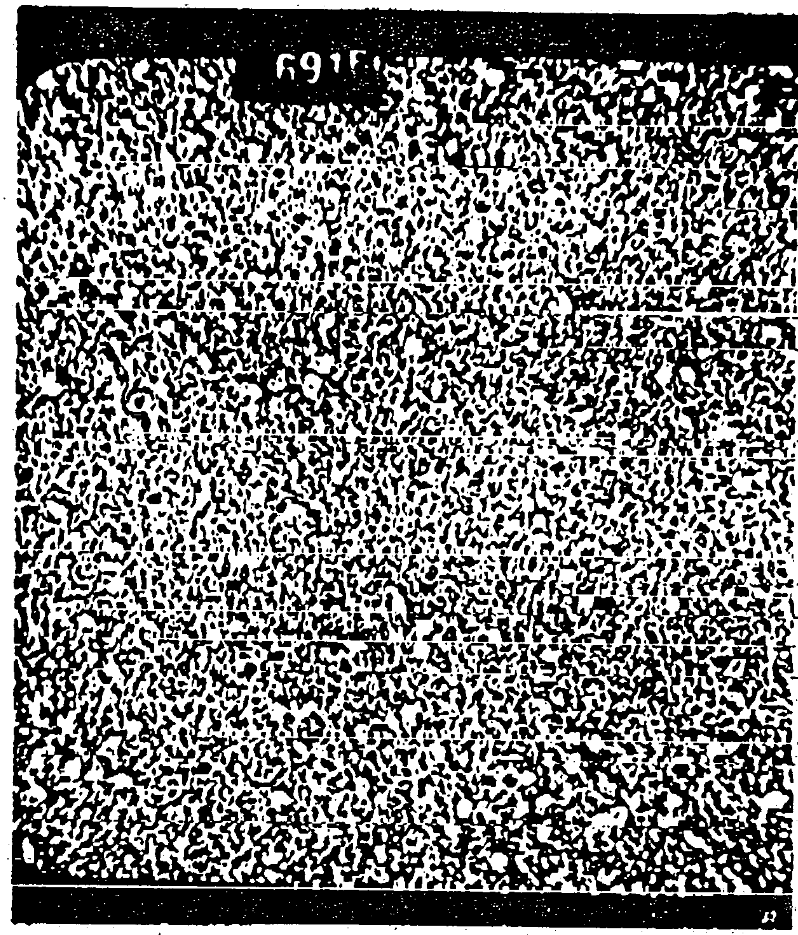


Fig.12

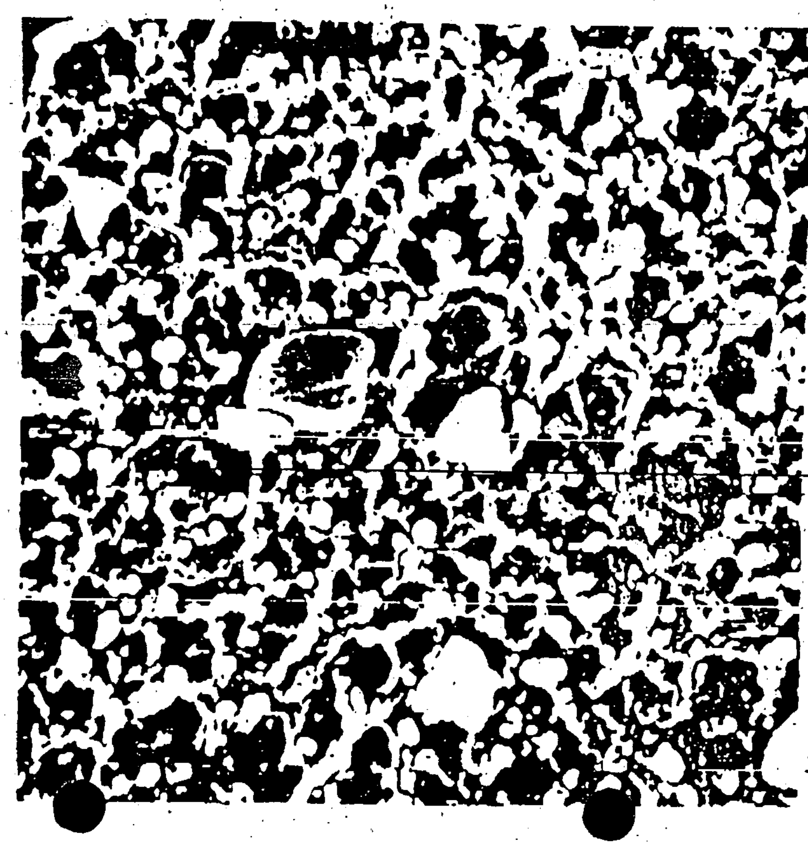


Fig.13

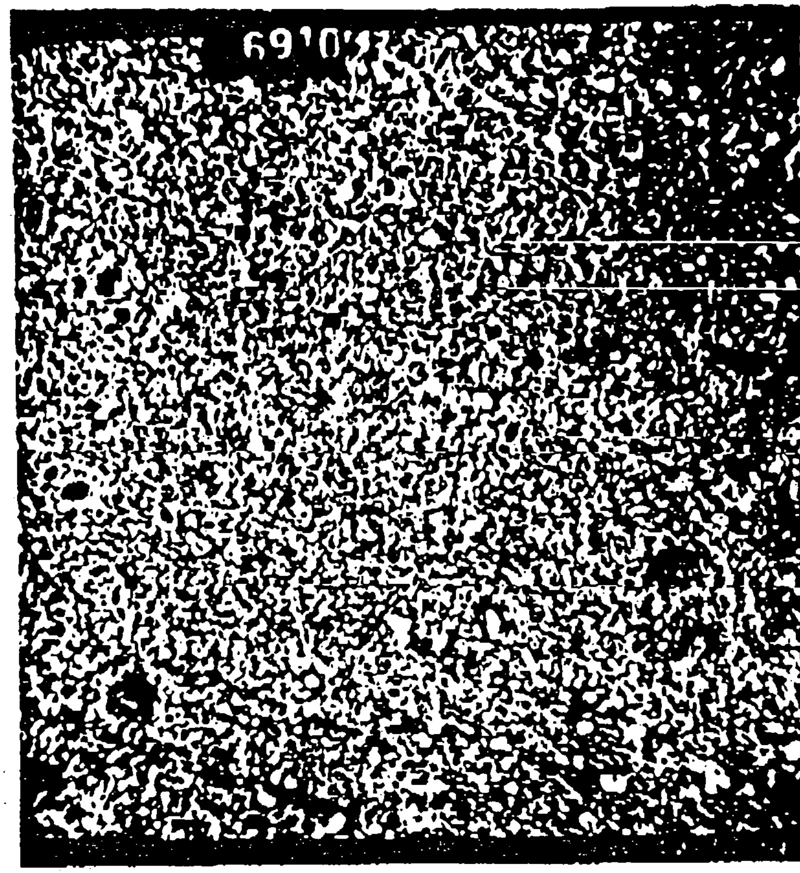
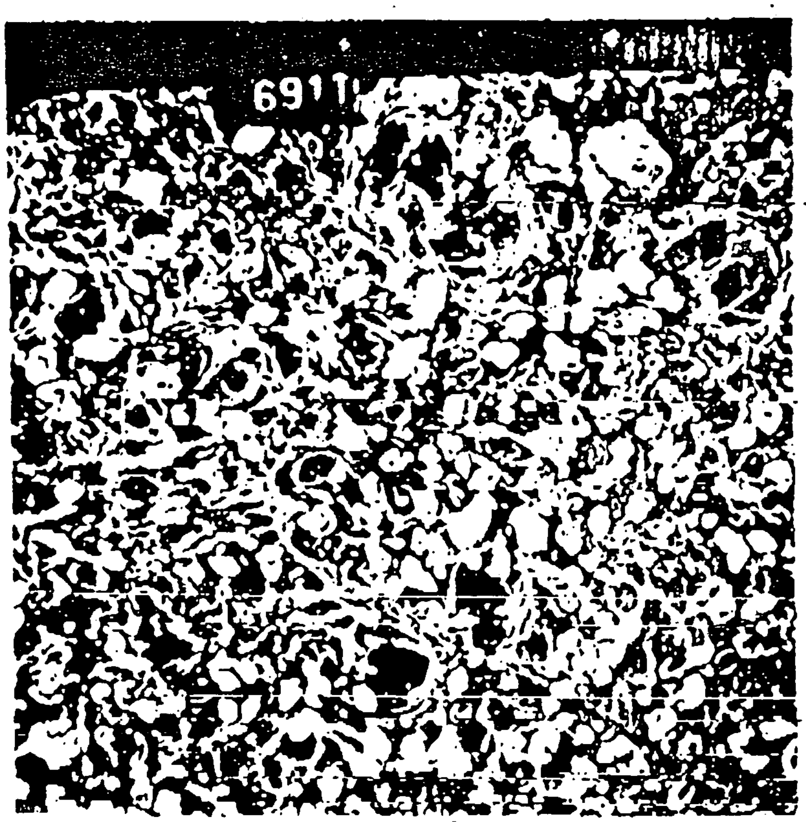


Fig.14



PECIFICATION

rocess for the production of filter elements based on polysulphone

his invention relates to the production of filter elements based on polysulphone, in the form of filter ıembranes, membrane/deep filter combinations or filter bodies by a process in which a semi-finished filter lement is formed from a solution of polysulphone containing a pore former and the polysulphone of this ɔmi-finished product is coagulated by immersion in a liquid bath.—

Such a process for the production of anisotropic membranes is known from European Patent Application 1 301 074.1/0036315. This process is said to be suitable for the production of filter membranes, filter ele- om polysulphone. For this purpose, a solution of polysulphone, molecular weight 3,500, in dimethyl ɪrmamide with the addition of isopropyl alcohol is shaped to form a membrane and immediately after it has een shaped or cast it is coagulated in water which is maintained at the surrounding temperature. This rocess, however, cannot be used for obtaining controlled and previously calculated or determined ɪoperties of the filter membrane as regards its porosity, pore size or cell structure. It is therefore proposed ı European Patent Application 81 301 074.1/0036315 to obtain different properties in the filter membranes y producing the filter membranes from different resins or resin mixtures. In particular, the process lsclosed in European Patent Application 81 301 074.1/0036315 can only be used for producing filter ıembranes with a highly anisotropic structure.

By contrast, it is an object of the present invention to provide a process for the production of olysulphone-based filter elements in which the nature of the cell structure and the porosity and pore size of ıe filter element can be predetermined by a simple and easily controlled modification of only a few process arameters independently of one another, and the nature of the cell structure can be controlled by different ɾocess parameters from those used for the porosity and pore size of the filter element.

To solve this problem in accordance with the invention, the proportions in which polysulphone, solvent ɪd pore former are mixed in the polysulphone solution are determined according to the desired porosity ɪd pore size of the filter element, and coagulation with stabilization of the filter element is carried out in the ɥuid bath over a period of about 30 seconds to 240 seconds.

at temperatures from below 0°C to about 15°C for forming filter elements with a pore size of from 0.1 nm ı 1 nm in the active separating layer for the separation of macromolecules by ultrafiltration or

at temperatures of about 15°C to 45°C for forming filter elements with an asymmetric cell structure and a ɔre size in the active filter layer of from 0.05 μm to 10 μm for separating particles by micro filtration or

at temperatures from about 45°C to 80°C for forming filter elements with a symmetric cell structure and a ɔre size of from 0.05 μm to 10 μm for the separation of particles by microfiltration

ɪd the filter element is then washed in at least one other liquid bath.

In the process according to the invention, therefore, the nature of the cell structure is determined mainly ʏ the temperature maintained in the coagulation and stabilization bath but the choice of the particular mperature has virtually no influence on the porosity or pore size in the filter element. The process :cording to the invention is particularly distinguished by the fact it is highly reproducible.

The invention provides a clear separation between control of the cell structure and control of the porosity ɪd pore size in the filter element. It has been found that the temperature control of the coagulation and abilization bath, which influences the nature of the cell structure, has no significant influence on the ɔrosity and pore size in the filter element. The latter features, which are important for the filter element, are ainly influenced by the composition of the polysulphone solution, in particular the proportions in which

One possible method of producing similar filter elements in accordance with the invention consists, for example, of forming the semi-finished filter element by impregnating a woven a non-woven web with the polysulphone solution containing pore former.

The semi-finished filter element may also be formed by extruding the polysulphone solution containing pore former to produce a film in the form of a band or tube.

According to another example of producing the desired filter elements, a coarsely porous filter body which has been produced by sintering or some other means is steeped in or impregnated with the polysulphone solution containing pore former to form a semi-finished filter element, which is then transferred to the liquid bath for coagulation and stabilization of the polysulphone filling, optionally after pre-strengthening of its polysulphone filling in air.

According to the invention, the coagulation and stabilization bath may consist of water. Various additives may be introduced into the water of the coagulation and stabilization bath, either singly or in combination, e.g. solvents and/or pore formers and/or alcohol. Thus the same solvent as that used for the polysulphone solution may be added to the coagulation and stabilization bath in quantities of from 5 volumes % to 20 volumes %, preferably about 10 volumes %. Furthermore, for example, the same pore former as that used in the polysulphone solution may be added in quantities of about 1 volume % to 35 volumes %, preferably 10 volumes % to 20 volumes %.

Ethyl alcohol may also be added to the water of the coagulation and stabilization bath in quantities of about 5 volumes % to 20 volumes %, preferably about 10 volumes %. Instead of ethyl alcohol, comparable quantities of isopropyl alcohol may be added to the water of the coagulation and stabilization bath.

Examples of the invention are described in more detail below with reference to the drawings, in which

Figure 1 is a graphic representation of the rates of flow of water through the membranes produced according to the invention, measured per unit surface area, in dependence upon the temperature of the coagulation bath used in the formation of the membrane;

Figures 2 to *7* are electron microscopic photographs of a filter membrane produced by the process according to the invention at a coagulation bath temperature of 12 C, and

Figures 8 to *14* are electron microscopic photographs of a filter membrane produced by the process according to the invention at a coagulation bath temperature of 50 C.

EXAMPLE 1

A polysulphone solution having the following composition:

EXAMPLE 2:

A polysulphone solution having the following composition:

15.3% by weight polysulphone, molecular weight 1700,
24.% by weight N methyl pyrrolidone as solvent and
60.7% by weight polyethylene glycol, molecular weight 400, as pore former

was cast on a smooth as in example 1 to form a layer having a thickness of about 200 μm to 300 μm (of wet film). After casting, the solution was kept in moist air (atmospheric humidity 50 to 60%) for about 30 seconds to 1 minute. The film obtained was then treated in a coagulation bath containing water as in Example 1, the bath being adjusted to different temperatures in successive experiments as indicated below to produce membranes with different properties:

Experiment 2.1 bath temperature 15°C
Experiment 2.2 bath temperature 20°C
Experiment 2.3 bath temperature 30°C
Experiment 2.4 bath temperature 40°C
Experiment 2.5 bath temperature 50°C
Experiment 2.6 bath temperature 70°C

Stable filter membranes were obtained in all the experiments after washing as in Example 1, and these membranes were then investigated for their characteristic properties.

Permeability of the filter membranes to water: The water permeability of the membranes was determined as a major indication of the cell structure, porosity and pore size. This was done by measuring the rate of flow of water through each membrane per unit surface area and unit time. Previously filtered, distilled water was used as test medium and the pressure drop across the membrane was adjusted to 0.9 bar.

In the graph of Figure 1, the rate of through-flow of water is given in

$$\frac{m1}{cm^2} \times min \times 10^{-3}$$

in dependence upon the temperature of the coagulation bath.

Figure 1 contains two graphs. The graph labelled "mixture 1" relates to filter membranes produced according to Example 1 while the graph labelled "mixture 2" relates to filter membranes produced according to Example 2.

Both graphs show that the relationship between the rate of through-flow of water and the temperature of the coagulation bath is virtually linear at temperatures from 10°C to about 40°C. The higher the temperature of the coagulation bath, the greater is the rate of flow of water through the membranes of both groups. At coagulation bath temperatures above 40°C, the rate of throughflow of water continues to increase with increasing temperature of the coagulation and stabilization bath but the rate of increase is less rapid than at temperatures up to 40°C of the coagulation and stabilization bath.

Electron microscopic photograph of the structure: Figures 2 to 14 are electron microscopic photographs of membranes produced from polysulphone solution according to Example 1. Figures 2 to 7 are electron microscopic photographs of a polysulphone filter membrane produced with the coagulation bath maintained at 12°C. Figure 2 shows a cross section through the edge of such a membrane in 480 times enlargement (479.6 times). As may be seen from Figure 2, the membrane 11 has a closed skin 12 on its upper side and underneath this a substructure 13 with finger shaped holes 14. Figure 3 shows a section of the skin 12 on the surface of the membrane 11 in 7500 times enlargement (7506 times). The structure of this surface skin is so dense that the membrane has all the properties of an ultra filtration membrane. The almost completely closed structure of the surface skin may be seen from Figures 4 to 6 which are electron microscopic photographs of the closed upper side of the filter membrane 11, Figure 4 being a 750 times enlargement (748 times), Figure 5 a 7500 times enlargement (7506 times) and Figure 6 a 15,000 times enlargement (15,012 times). These electron microscopic photographs on different scales show, in conjunction with Figures 2 and 3, that a virtually pore-free surface layer is formed, which is impermeable to water used as test medium. As may be seen from Figure 1, virtually complete imperviousness of the surface

Figures 8 to 14, by contrast, show a filter membrane with an almost symmetrical porous structure produced according to experiment 1.4 of Example 1, namely with the coagulation and stabilization bath maintained at a temperature of 50°C. Filter membrane 21 obtained in this manner is a typical micro filtration membrane, i.e. a membrane which has an almost symmetrical porous structure throughout its thickness between the two surfaces 22 and 23.

Figure 8 is an electron microscopic photograph showing this microfiltration membrane 21 in cross section through an edge enlarged 740 times (740 times). It may be seen from Figure 8 that the pores are possibly slightly smaller in the region of the upper surface 22 than in the region of the lower surface 23 but it is clear that the pore structure is substantially symmetrical throughout. The fact that the differences in pore size between the region of the upper surface 22 and the region of the lower surface 23 are only slight is evident from a comparison of Figures 9 and 10 which are electron microscopic photographs of edge cross sections through the microfiltration membrane 21, Figure 9 being taken in the region of the upper surface 22 and Figure 10 in the region of the lower surface 23.

Figure 11 is an electron microscopic photograph of the microfiltration membrane 21 of Figure 8 taken from the upper surface, i.e. showing the upper surface 22 in 1100 times enlargement (1100 times). It may be seen from Figure 11 that the pores of the microfiltration membrane 21 open on to the upper surface of the membrane. A comparison with Figure 13 shows that virtually the same conditions also prevail on the lower surface of the microfiltration membrane 21. If one takes into account that Figure 13 is an electron microscopic photograph of the underside of the membrane enlarged 750 times (750.75 times), the comparison between Figures 11 and 13 reveals that the openings of the pores on the underside of the microfiltration membrane 21 are not significantly larger than on the upper side. Figure 12 is an electron microcopic photograph of the upper side of the microfiltration membrane 21 of Figure 8 enlarged 7500 times (7480 times) and shows a more or less regular framework structure of the membrane matrix. The structure of the matrix on the underside of the membrane 21, on the other hand, is slightly less regular, as may be seen from Figure 14 (electron microscopic photograph in 3000 times enlargement (2945.8 times)). However, no significant difference in porosity and pore size can be detected between Figures 12 and 14.

The film thicknesses given in connection with the exemplary embodiments described above and the casting speeds of from 0.5 m to 1.0 m per minute provided in these examples depend to a certain extend on the construction and dimensions of the laboratory installations used for carrying out the experiments. Whereas a final membrane thickness of about 70 µm, which is the value which can be achieved in such installations, is sufficient for ultra-filtration membranes, the possibility of also obtaining greater thicknesses would be desirable for symmetric membranes, and this may be achieved by suitable design of the production plant.

CLAIMS

1. Process for the production of filter elements based on polysulphone, in the form of filter means selected from filter membranes, membranes deep filter combinations or filter bodies, in which process a semi-finished filter element is formed from a solution of polysulphone containing a pore former and the polysulphone of this semi-finished product is coagulated by immersion in a liquid bath, wherein the proportions in which polysulphone, solvent and pore former are mixed in the polysulphone solution are adjust d according to the desired porosity and pore size of the filter element, and wherein coagulation with stabilization of th filter element is carried out in the liquid bath for a period of about 30 seconds to about 240 seconds and

a) at a temperature from below 0°C to about 15°C for forming filter elements having a pore size of from 0.1 nm to 1 nm in the active separating layer for separating macromolecules by ultra filtration or

b) at temperatures from ab ut 15 C to about 45 C for forming filter elements with an asymmetric cell structure and a pore size of the active separating layer from 0.05 µm to 10 µm for separating particles by microfiltration or

c) at temperatures in the range from ab ut 45 C to 80 C for forming filter elements with a symmetric cell structure and pore size of from 0.05 µm to 10 µm for separating particles by microfiltration

6. Process according to any one of the claims 1 to 3, wherein the semi-finished filter element is formed by impregnating a woven or non-woven web with the polysulphone solution containing pore former.

7. Process according to any one of the claims 1 to 3, wherein the semi-finished filter element is formed by extruding the polysulphone solution containing pore former to form a band or tube of film.

8. Process according to any one of the claims 1 to 3, wherein the semi-finished filter element is formed by soaking or impregnating a coarse porous filter body produced by sintering or some other means with the polysulphone solution containing pore former and wherein this semi-finished filter element is transferred to the liquid bath for coagulation and stabilization of the polysulphone filling, optionally after prestrengthening of its polysulphone filling in air.

9. Process according to any one of claims 1 to 8, wherein the coagulation and stabilization bath contains water with the addition of solvents and/or pore formers and/or alcohol.

10. Process according to claim 9, wherein the coagulation and stabilization bath contains an addition of the same solvent as that used for the polysulphone solution, in quantities of from 5 volumes % to 20 volumes %, preferably about 10 volumes %.

11. Process according to claim 9 wherein the coagulation and stabilization bath contains an addition of the same pore former as the polysulphone solution in quantities from about 1 volume % to 35 volumes %, preferably from 10 volumes % to 20 volumes %.

12. Process according to one of the claims 9 wherein the coagulation and stabilization bath contains an addition of ethyl alcohol in quantities of from 5 volumes % to 20 volumes %, preferably about 10 volumes %.

13. Process according to one of the claims 9 wherein the coagulation and stabilization bath contains an addition of isopropyl alcohol in quantities from about 5 volumes % to 20 volumes %, preferably about 10 volumes %.

14. Process according to claim 1 wherein washing with water is carried out in one or more baths at temperatures from 20°C to 40°C over a period of from 30 minutes to several hours.

15. Process according to claim 1 wherein a mixture is prepared from 10 to 18% by weight of polysulphone, having a molecular weight of 1700 22 to 28% by weight of N-methylpyrrolidon as solvent the remainder being polyethylene glycol having a molecular weight of 400, as pore former, a semi-finished product having the form of the desired filter element is produced from this polysulphone solution, this semi-finished product is prestrengthened in moist air for a period of from 30 to 60 seconds, the semi finished product is then coagulated and stabilized in a liquid bath which is maintained at a temperature selected according to the desired structure of the filter element to be produced, and the filter element is then washed in water.

16. Process according to claim 15, wherein the polysulphone solution is poured out to form a layer having a thickness of 200 μm or more (thickness of the wet layer) to produce filter membranes